

# Reactivity of $\text{CF}_n$ ( $n=1-3$ ) radicals with a silica surface

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## Abstract

The trends in reactivity of  $\text{CF}_n$  radicals with  $\text{SiO}_2$  and the site selectivity of the attack are studied using two different cluster models. The reaction barriers for the most energetically favorable reaction are computed. It is shown that  $\text{CF}_n$  radicals are fairly unreactive towards  $\text{SiO}_2$ .

keywords: clusters; Density functional theory; Surface chemical reaction; Silicon oxides

## I. INTRODUCTION

Etching of  $\text{SiO}_2$  using fluorocarbon plasmas involves several neutral as well as charged species. Radicals such as  $\text{CF}_3$ ,  $\text{CF}_2$ , and  $\text{CF}$  are expected to play an important role. Several experimental studies have been performed to determine the reactivity of  $\text{CF}_2$  and  $\text{CF}_3$ . An early experiment by Brannon [1] showed that, in the presence of an intense photon field,  $\text{CF}_2$  radicals, from photolyzed  $\text{CF}_2\text{Br}_2$ , are capable of etching silicon dioxide. However a more recent study by Langan *et al.* [2] determined that laser-generated  $\text{CF}_2$  adsorbs on silicon dioxide surfaces, but does not dissociate or etch the  $\text{SiO}_2$  surface. They also showed that ion bombardment leads to a loss of adsorbed  $\text{CF}_2$  instead of a fluorine transfer reaction at the surface. Butterbaugh *et al.* [3]

simulated the major species present in fluorocarbon plasmas using F and CF<sub>2</sub> beams and a beam of Ar<sup>+</sup>. They concluded that energetic Ar<sup>+</sup> bombardment enhances the etching yield of SiO<sub>2</sub> for both CF<sub>2</sub> and F. However, when CF<sub>2</sub> and F beams are used simultaneously, F dominates and CF<sub>2</sub> has little effect. Robertson *et al.* [4] investigated the reactions of CF<sub>3</sub>, generated from CF<sub>3</sub>I by IR-multiphoton decomposition, with SiO<sub>2</sub> surfaces. Their results showed that no spontaneous etching occurs. Similar conclusions were obtained by Joyce *et al.* [5] who also showed that sputtering the oxide surface by argon ion bombardment increases the amount of radicals that can be adsorbed. Overall the reactivity of CF<sub>3</sub> appears to be below experimental detection limits [3] and adsorbed CF<sub>3</sub> appears to be mainly bound to O atoms of SiO<sub>2</sub> [6].

A theoretical study of the reactivity of CF<sub>n</sub> ( $n=1-4$ ) radicals with SiO<sub>2</sub> has been performed by Jenichen [7] using ab initio methods and cluster models. The work assumes that CF<sub>n</sub> species form O-C bonds and focuses on the breaking of a Si-O bond with simultaneous transfer of a F atom to a Si atom via a cyclic transition state.

At the present time the trends in reactivity of CF<sub>n</sub> radicals with SiO<sub>2</sub> are not fully understood and the preferred sites of attack need to be confirmed based on relative energies. Reaction barriers are also of interest.

In the present work we use Density functional theory (DFT), in conjunction with the cluster model approach, to investigate the energetics of several reactions of CF<sub>n</sub> ( $n=1-3$ ) radicals with SiO<sub>2</sub> models and the reaction barriers for some key reactions.

## II. METHODS

At the surface, the SiO<sub>2</sub> structure terminates in either a siloxane group (SiOSi) or a silanol group (SiOH). We model the silanol surface group using Si(OH)<sub>4</sub> (see Fig. 1a) and the siloxane group using (HO)<sub>3</sub>SiOSi(OH)<sub>3</sub> (see Fig. 1b).

All the geometries are fully optimized using the hybrid [8] B3LYP [9] approach,

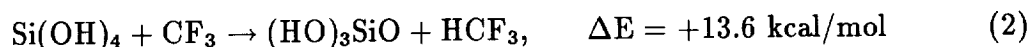
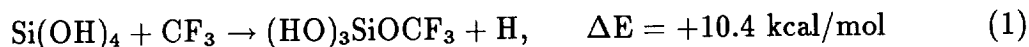
in conjunction with the 6-311++G\*\* basis set [10]. The harmonic frequencies are computed to determine if the structures are at local minima or saddle points and to obtain the zero-point energies. The search for the transition state (TS) geometries is aided by computing the force constants at every point to ensure the correct curvature. The energetics of the reactions are computed at the B3LYP/6-311++G\*\* level of theory. All of the B3LYP calculations are performed using Gaussian94 [11].

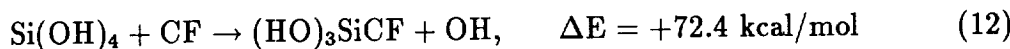
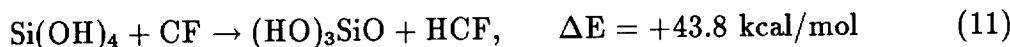
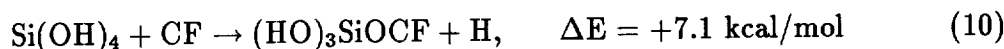
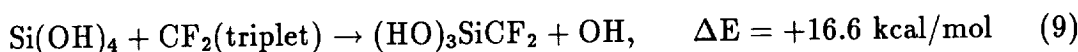
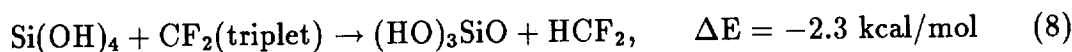
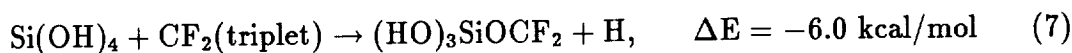
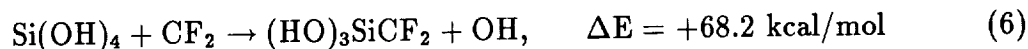
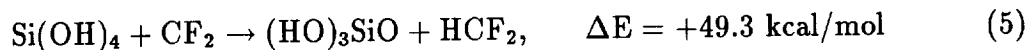
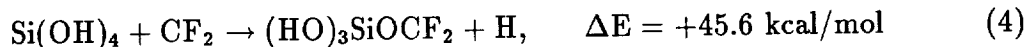
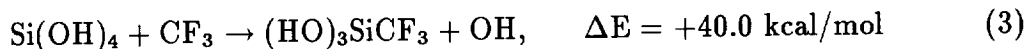
### III. RESULTS AND DISCUSSION

We first consider the reactions of the  $\text{CF}_n$  ( $n=1-3$ ) radicals with the simplest model,  $\text{Si}(\text{OH})_4$ . This model, which is too simple to represent the real  $\text{SiO}_2$  surface, is nevertheless sufficient to provide relative energies and trends in reactivity. Three of the OH groups are considered to be part of the surface and the fourth OH is used to model the surface OH.

For  $\text{CF}_3$  the ground state (GS) is a doublet state ( $^2A_1$ ) with  $C_{3v}$  symmetry while for  $\text{CF}_2$  the ground state is a singlet state ( $^1A_1$ ) with  $C_{2v}$  symmetry. The lowest  $\text{CF}_2$  triplet state ( $^3B_1$ ) lies 51.7 kcal/mol (2.24 eV) above the  $^1A_1$  state. For CF the ground state is a doublet state  $^2\Pi$  and the nearest quartet state ( $^4\Sigma^-$ ) is 83.9 kcal/mol (3.64 eV) higher in energy. Because of the high energy separation between the doublet and quartet states for CF we only study the reactions of CF  $^2\Pi$  whereas for  $\text{CF}_2$  we study both the reactions of the  $^1A_1$  and  $^3B_1$  states.

We consider three possible sites of attack on  $\text{Si}(\text{OH})_4$  by the carbon atom of  $\text{CF}_n$ : 1) the O atom of the surface OH, 2) the H atom of the surface OH, and 3) the Si atom. The reactions studied and their corresponding energetics are reported in Eqns 1-12. The  $\text{CF}_n$  species are in their ground state unless reported otherwise.

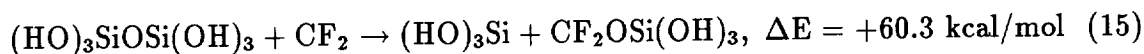
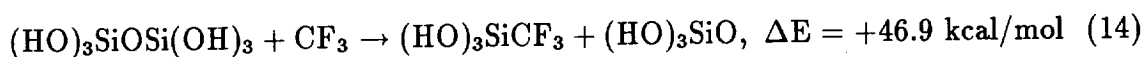
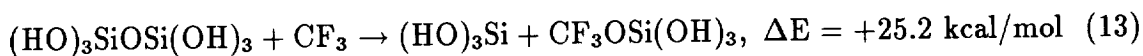




A comparison of the various energies shows that for all  $\text{CF}_n$  species the most energetically favorable reaction corresponds to the attack of the O atom with concomitant breakage of the O-H bond. On the other hand the attack of the Si atom is the least favorable energetically. These results are in agreement with the experiments of McFeely *et al.* [6]. All the reactions for the  $\text{CF}_n$  species in their ground states are endothermic and therefore are only important at high temperatures or if energy is added by ion bombardment.  $\text{CF}_3$  and CF have very similar reaction energies with respect to the attack of the O atom and their reactions are the most favorable energetically. However, for the attack of the H atom,  $\text{CF}_3$  and CF behave differently, with  $\text{CF}_3$  being considerably less acidic than both CF and  $\text{CF}_2$ .  $\text{CF}_2$  in its ground state is very unreactive due to the fact that in its singlet state it cannot form a bond without promotion from the singlet state to the triplet, which requires 51.7 kcal/mol (2.24 eV).

As a second step we consider the reactions of the  $\text{CF}_n$  ( $n=1-3$ ) radicals with the  $(\text{HO})_3\text{SiOSi}(\text{OH})_3$  model. Two possible sites of attack by the C atom of  $\text{CF}_n$  are

considered: 1) the O atom of the siloxane (Si-O-Si) group and 2) the Si atom. The reactions investigated and their corresponding energetics are reported in Eqns 13-16. The  $\text{CF}_n$  species are in their ground state unless reported otherwise.



The results show that the attack of the O atom in the Si-O-Si group with concomitant breaking of the Si-O bond is less favorable energetically than the attack of the O atom in the surface OH group of  $\text{Si}(\text{OH})_4$  with concomitant breaking of the O-H bond due to a greater bond strength of Si-O compared with O-H. The attack of the Si atom in the SiOSi group by  $\text{CF}_3$  is slightly less favorable than the attack of the Si atom in the SiOH group but still comparable in energy. This result confirms that the attack of the Si atom is energetically unfavorable.

The energy barriers for the reaction of  $\text{Si}(\text{OH})_4$  with  $\text{CF}_n$  ( $n=1-3$ ) are reported in Table I. The energy barrier varies as a function of the fluorocarbon group as follows:



The high energy barrier for  $\text{CF}_2$  is not surprising as the reactions of  $\text{Si}(\text{OH})_4$  with  $\text{CF}_2$  in its ground state are very endothermic (see Eqns (4)-(6)). It is however interesting to note that  $\text{CF}_2$  in its triplet state also has a large barrier. We can therefore conclude that  $\text{CF}_2$  is unreactive towards  $\text{SiO}_2$ . CF has the lowest energy barrier and it is more reactive than  $\text{CF}_3$ . However the energy barrier for CF is still fairly high and it is unlikely that CF would react with  $\text{SiO}_2$  at moderate temperatures.

The transition state geometries for the reactions reported in Eqn. (1), (4) and (10) are shown in Figs 2-4. For CF (see Fig. 2) and  $\text{CF}_2$  (see Fig. 3) the TS has a

product-like structure in agreement with the fact that the energy barrier going from the products to the TS ( $\Delta E_P$ ) is the smallest for CF and CF<sub>2</sub>. For CF<sub>3</sub> (see Fig. 4) the TS structure is the average between the structure of the reactants and of the products in agreement with similar values for  $\Delta E_R$  and  $\Delta E_P$ .

We can conclude from both the reaction energetics and the barriers that CF<sub>n</sub> radicals are quite unreactive towards SiO<sub>2</sub> in agreement with experimental results which showed that no spontaneous etching of SiO<sub>2</sub> occurs using only fluorocarbon plasmas. The lack of dangling bonds on the SiO<sub>2</sub> surface inhibits reactions with radicals. Ion bombardment can produce dangling bonds at the surface by breaking Si-O bonds and therefore increases the reactivity of CF<sub>n</sub> radicals with the SiO<sub>2</sub> surface. Ion bombardment can also provide the necessary energy to drive the endothermic reactions.

#### IV. CONCLUSIONS

CF<sub>n</sub> radicals are fairly unreactive towards SiO<sub>2</sub>. All the reactions for CF<sub>n</sub> systems in their ground states are endothermic. The most energetically favorable reaction corresponds to the attack of the O atom in the surface OH group of Si(OH)<sub>4</sub> by the C atom of CF<sub>n</sub>. The reactivity of the CF<sub>n</sub> radicals in their ground states follows the order: CF > CF<sub>3</sub> > CF<sub>2</sub>. CF<sub>2</sub> is very unreactive due to the fact that its singlet state cannot readily form a bond without promotion to a higher triplet state. CF has the lowest energy barrier and it is more reactive than CF<sub>3</sub>.

#### V. ACKNOWLEDGMENTS

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# TABLES

TABLE I. Energy barrier (kcal/mol) for the reaction of  $\text{Si(OH)}_4$  with  $\text{CF}_n$  ( $n=1-3$ ) leading to  $(\text{HO})_3\text{SiOCF}_n + \text{H}$  computed using B3LYP/6-311++G\*\* and with zero-point energy correction. The  $\text{CF}_n$  species are in their ground state unless reported otherwise.

Fluorocarbon	$\Delta E_R^a$	$\Delta E_P^b$
$\text{CF}_3$	46.5	36.1
$\text{CF}_2$	58.0	12.4
$\text{CF}_2$ (triplet)	32.9	38.9
$\text{CF}$	22.4	15.3

<sup>a</sup>  $\Delta E_R$  means that the energy barrier is from the reactants to the transition state.

<sup>b</sup>  $\Delta E_P$  means that the energy barrier is from the products to the transition state.

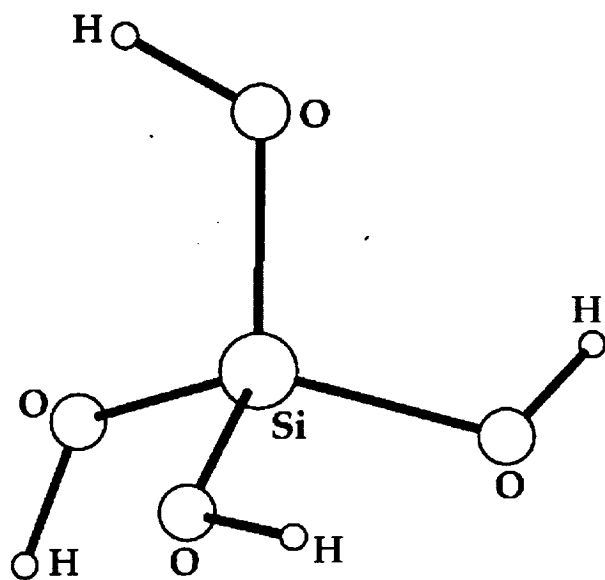
## FIGURES

FIG. 1. Geometric structure of the  $\text{SiO}_2$  models: (a)  $\text{Si}(\text{OH})_4$ ; (b)  $(\text{HO})_3\text{SiOSi}(\text{OH})_3$ .

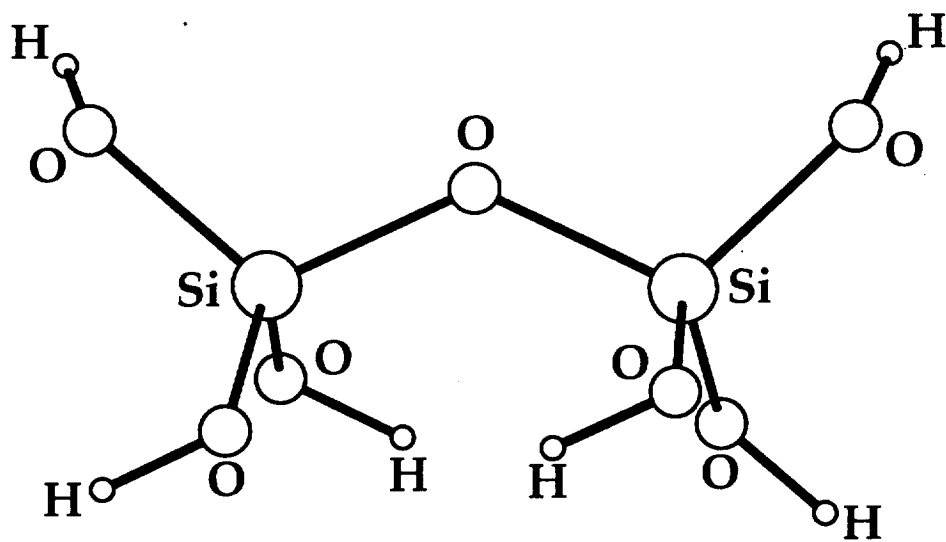
FIG. 2. Transition state geometry for the reaction of  $\text{Si}(\text{OH})_4$  with  $\text{CF}$  (in its ground state) leading to  $(\text{HO})_3\text{SiOCF} + \text{H}$ . The bond lengths are in angstroms.

FIG. 3. Transition state geometry for the reaction of  $\text{Si}(\text{OH})_4$  with  $\text{CF}_2$  (in its ground state) leading to  $(\text{HO})_3\text{SiOCF}_2 + \text{H}$ . The bond lengths are in angstroms and the bond angles in degrees.

FIG. 4. Transition state geometry for the reaction of  $\text{Si}(\text{OH})_4$  with  $\text{CF}_3$  (in its ground state) leading to  $(\text{HO})_3\text{SiOCF}_3 + \text{H}$ . The bond lengths are in angstroms and the bond angles in degrees.

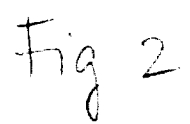


**a**



**b**

Fig. 1



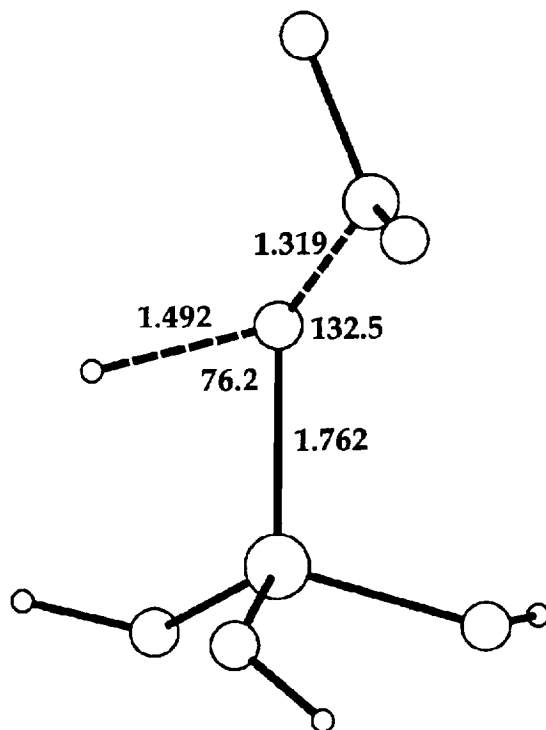
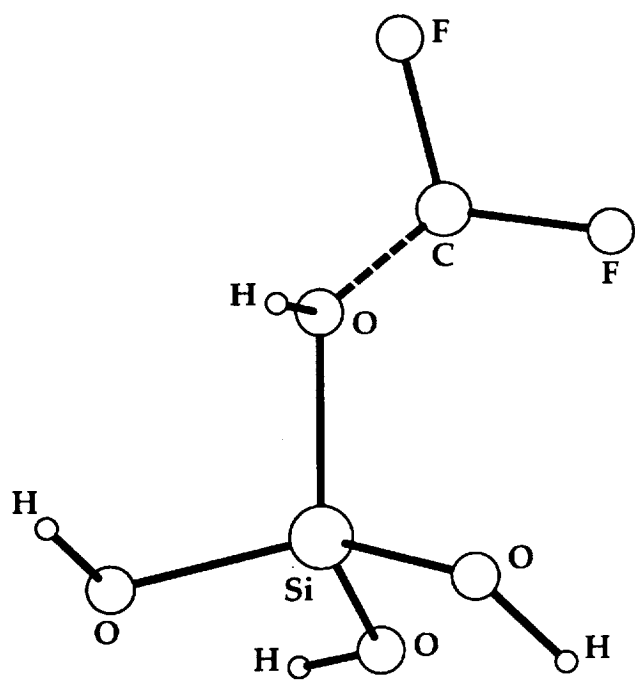


Fig 3

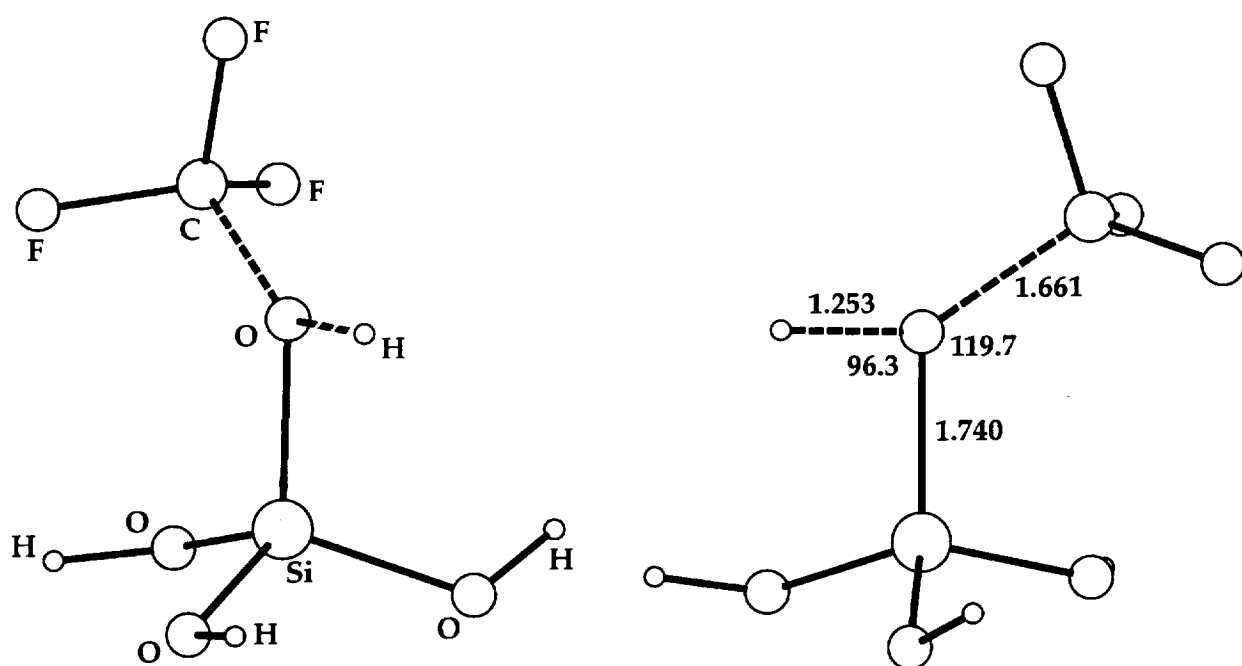


Fig 4